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The spatial and seasonal variation of nitrogen dioxide and sulfur dioxide in Cape Breton Highlands National Park, Canada and the association with lichen abundance

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ABSTRACT

Over 200,000 tourists per year visit Cape Breton Highlands National Park, Nova Scotia, Canada. The forests within the park are home to many rare epiphytic lichens, the species diversity of which has declined in some areas. The primary motivation for this study was to gain insight into the concentrations and potential local and long-range sources of air pollution, but its association with lichen species diversity was also examined. Ogawa passive diffusion samplers were used to measure nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) in the park at 19 sites in the winter and 20 sites in the summer of 2011. An improvement in the sensitivity of the sampler analytical protocol was developed. The mean concentrations in the park of winter and summer NO_2 (0.81 and 0.16 ppb) and SO_2 (0.24 and 0.21 ppb) are not at levels known to be phytotoxic to lichen. The NO_2 concentrations in winter were significantly ($p = 0.001$) higher than those in summer whilst the SO_2 concentrations did not differ significantly between winter and summer (p=0.429). Highest NO_2 concentrations in both seasons were observed in the Grand Anse Valley, presumably due to the steep road, emissions from the Pleasant Bay community at the foot of the valley and the enclosed topography of this area reducing dispersion of primary emissions. The SO_2 concentrations in the park tended to be greater at elevated sites than valley sites, consistent with dispersion from long-range, rather than local, sources for this pollutant. Significant predictors in a multilinear regression for an index of air purity (lichen based measure of air quality) were lichen species number ($p = 0.009$), forest old growth index ($p = 0.001$) and distance from roads ($p <0.001$) (model $R^2 = 0.8$, model $p = 0.004$). The study suggests that local sources of pollution (roads emissions) are adversely associated with lichen species diversity in this National Park, compared with long-range transport, and that monitoring programs such as a lichen-based 'index of air purity' can reveal locations where ambient air pollution, although low,

is nevertheless at a level that may cause ecological detriment. The implications from this work could be applicable to national parks elsewhere.

Keywords: Cape Breton Highlands National Park, Canada, NO_2, SO_2, Ogawa Passive Diffusion Sampler, Lichen, Index of Air Purity

1. Introduction

Cape Breton Highlands National Park (Figure 1) was established in the early 20th century to protect 950 km^2 of the Maritime Acadian Highlands natural region of Nova Scotia, Canada (Parks Canada, 2010b). The park is located in northern Cape Breton Island and is bordered on the west by the Gulf of St. Lawrence, on the east by the Cabot Strait and joined to the Nova Scotia mainland by the Canso causeway. A year round paved highway (the Cabot Trail) traverses the park's steep topography. The park is enjoyed by over 200,000 visitors per year; most visiting from the months of June to October (Parks Canada, 2010a, 2010b). Winter in Cape Breton spans the months of November through to April. Winter recreation use of the park is low and is primarily by local residents who use the park for cross-country skiing and snow shoeing (Parks Canada, 2010b). The park plateau is dominated by coniferous boreal and taiga vegetation and the lowlands by deciduous forest. Some of the old growth deciduous stands in the park are over 350 years old (Parks Canada, 2010b).

Many species of cyanolichens (lichens containing cyanobacteria) are known to be sensitive indicators of air pollution (Cameron, 2002). The absence of many lichens that would be expected in the old growth forest of the National Park was first noted by Selva (1999) in the Grande Anse

Valley. Recent analyses of lichen species density using a lichen-based Index of Air Purity (IAP) (Asta et al., 2002, Cameron 2004, Will-Wolf and Neitlich 2010), and a Modified Hilsenhoff Biotic Index (MHBI) that used lichen pollution tolerance values from regional literature (Hilsenhoff, 1982; Brodo et al., 2001; Hinds and Hinds, 2008), has also flagged several areas in the park below expected lichen species biodiversity.

The motivation for this study was to determine the potential impact of local and regional sources of air pollution on air pollution levels in two seasons in this previously unmonitored National Park amenity and the observational associations of these levels with lichen species abundance. Nitrogen dioxide (NO_2) was chosen as a good marker for vehicle and local combustion sources such as wood smoke (Heal et al., 1999, Ward et al., 2012). NO_2 in the atmosphere primarily arises from rapid oxidation of the NO formed from nitrogen in the air-fuel mix during combustion for transport, heat and power. Some NO_2 is also emitted directly from combustion (Finlayson-Pitts and Pitts 1999; Heal et al., 1999). Sulfur dioxide (SO_2) was chosen as a good marker for point and transitory regional upwind sources of sulphur fuel combustion (Wheeler et al., 2011, Corbett et al., 2007). SO_2 is formed from oxidation of sulfur within the fuel itself, e.g. ship fuel oil and power station coal (Poplawski et al., 2011; Riga-Karandinos and Karandinos, 1998). Shipping around the coast of Cape Breton Island currently uses 1% S-fuel (Lack et al., 2011). The Canadian National Pollution Release Inventory database (2010) indicates that NO_2 and SO_2 emissions from the Lingan and Port Aconi Power Stations near Sydney, Cape Breton (~60 km SE of the park) are 5,219 and 33,479 tonnes/year and 1,747 and 3,365 tonnes/year respectively (NPRI, 2010). NO_2 and SO_2 emissions from the Point Tupper Power Station and

NewPage Paper Mill near Port Hawkesbury, Cape Breton (~120 km SW of the park) are 1,952 and 5,721 tonnes/year and 306 and 85 tonnes/year respectively (NPRI, 2010).

A large body of research over the last 50 years has shown strong negative correlations between epiphytic lichen abundance and diversity and ambient concentrations of SO_2 and NO_2 (Tiwary and Colls, 2010). Lichens have therefore been used in many studies as bioindicators of SO_2, NO_2 and other air pollutants and their deposition (Van Dobben et al., 2001). Sulfur dioxide fumigation over a 24-h period at a concentration of 4 ppm has been observed to be directly phytotoxic to a wide variety of lichen species (Nash-III, 1973). Typical rural ambient levels of SO_2 measured at Government monitoring stations outside of the park rarely exceed 5 ppb, so direct toxicity is unlikely. Prior to the study, ambient NO_2 and SO_2 concentrations in the park were unknown. Nitrogen dioxide is only directly phytotoxic to higher plants at concentrations of 0.3 ppm but also different species of lichen at concentrations of 1 ppm (6-h fumigations) (Nash-III, 1976), or at ambient concentrations over 22 ppb (Marmor and Randlane, 2007). The latter is generally only observed in larger Canadian cities (Atari et al., 2008).

While individually, NO_2 and SO_2 ambient concentrations in clean environments do not appear to pose a direct phytotoxic threat to lichen abundance, their synergistic deleterious effects have been observed (Nash-III, 1976). Aside from direct phytotoxicity, SO_2 and NO_2 emissions also produce secondary H_2SO_4 and HNO_3 which acidify tree bark and change the substrate chemistry upon which lichens depend for growth (Will-Wolf and Neitlich, 2010). The majority of trees retain their bark, so once acidified bark pH remains low which in turn reduces the abundance and re-colonization of sensitive species of lichen (Marmor and Randlane, 2007). Therefore, NO_2 and

SO_2 are mainly toxic to lichen indirectly rather than through direct primary phytotoxicity (Bell and Treshow, 2003; Conti and Cecchetti, 2001). Other phytotoxic air pollutants known to impact lichen include ammonia, ammonium ions and ozone (Geiser and Neitlich, 2007, Geiser et al., 2010).

This study utilised two-sided Ogawa passive diffusion samplers (PDS) (Ogawa & Co., Pompano Beach, FL, USA) loaded with one filter pad that collected both NO_2 and SO_2. Two filter pads were loaded into the Ogawa sampler for the duplicate sample. These were placed at long-term forest monitoring locations and roadside sites in the National Park. Measurements were made at the same locations in both winter and summer in almost all instances. Sampling NO_2 and SO_2 spatially and in contrasting seasons provided information on the sources of NO_2 and SO_2 and of the potential impact on lichen abundance from local combustion and long-range air pollutants. The utility of PDS is that they do not require power, an essential requirement for this study, and large numbers can be deployed simultaneously to obtain information on spatial concentration fields (Gibson et al., 2009). Their disadvantages include poorer temporal resolution and potential for positive and negative biases, for example due to variations in wind speed, temperature and relative humidity (Krupa et al., 2003). Ogawa PDS have been used in many spatial studies of air quality (Bytnerowicz et al., 2002b; Meng et al., 2010; Wheeler et al., 2011) and the effect of NO_2 and SO_2 on vegetation growth (Conti and Cecchetti, 2001; Cox, 2003).

In order to predict the IAP in other regions of the park, a multivariate regression model was developed. The independent variables investigated included wind direction, wind speed, rainfall, temperature, relative humidity, NO_2, SO_2, biological data (e.g. lichen species number) and

physical data (e.g. distance from roads). This model could also have application to similar remote locations elsewhere.

2. Material and methods

2.1 Study area and sampling

The study area and locations of the sites used for the winter and summer NO_2 and SO_2 sampling are shown in Figure 1. Table 1 provides site names, descriptions and lat-long coordinates. The Ogawa PDS were deployed in the park in the periods March 15 to April 5, 2011 (winter) and August 4 to September 13, 2011 (summer), in staggered exposures of approximately 14-days duration. The remoteness of some sites prevented deployment of all PDS simultaneously. PDS were placed in the vicinity of locations (n = 11) used to create the lichen-based index of air purity (IAP) which is described in section 2.2. Twenty PDS were deployed during the winter with site A01BJ lost due to moose interference (as evidenced by moose hairs). Twenty PDS were deployed in the summer. Due to greater accessibility of more remote locations in the park, site A01BR was added in the summer. Site A01CH was sampled in the winter but not the summer. Duplicate PDS were exposed at site A01GA in both winter and summer.

2.2 Index of Air Purity

The lichen monitoring plots in the park are co-located with forest monitoring plots in mature hardwood forests dominated by yellow birch (*Betula alleghaniensis*) or sugar maple (*Acer saccharum*). Four plots were located in an important old growth forest of the park (the Grande Anse Valley). Past work by Selva (1999) indicated an impoverished lichen community compared to other old growth forests in the region and suggested that the steep road grade and tourist

vehicle traffic might be influencing air quality. In addition, the park is not adjacent to any permanent air quality monitoring sites, so knowledge about localized air pollution was lacking. Therefore the Park authority established twelve lichen monitoring sites in the park to sample different airsheds. The methods used are derived from similar lichen IAP studies conducted in Canada and elsewhere (Asta et al. 2002; Cameron 2004; McMullin & Ure 2008; Richardson 1992). At each plot, the lower bole of twelve randomly selected maple trees (*Acer saccharum* or *Acer rubrum*) located outside the vegetation plot (20 m x 20 m) were sampled at breast height. The three closest healthy maple trees to the outside edge of the forest plot were selected. If no trees were found within a reasonable distance, then an additional tree could be selected from another side of a plot. Only trees that were ≥ 40 cm circumference were chosen to allow for establishment time of some of the sensitive lichens. Species identifications were restricted to macrolichens that were field identifiable. A tag and nail was established at the base of the tree at a 50 cm height above the ground for future surveys. A tape was then placed at 150 cm above this marker (~2 m above the ground). A 10 cm x 50 cm "ladder" with five cells was then hung from 200 cm to 150 cm. Each tree was sampled in each cardinal direction (N, S, E, W). The lichen species present in each of the 10 x 50 cm cells were recorded. The IAP is based on the frequency of pollution intolerant (sensitive) lichen species in the cells. The formulae for calculating the IAP are comparable to McMullin and Ure (2008). The basis of the index is the summation of the frequency of pollution intolerant lichen species in each plot,

$$\text{Index of Air Purity (IAP)} = \sum_{i=1}^{n} f_i \qquad (1)$$

where f is the species frequency at a plot between 0 and 1, derived as the number of ladder cells in which a particular species is found divided by the total number of cells at a plot, and n is the number of pollution intolerant lichen species (McMullin and Ure, 2008). For example, if

Lungwort (*Lobaria pulmonaria*) occurs in 50% of 240 cells at a site then the IAP would be 0.5 for that site. If an additional 50% of the 240 cells at a site contained a Jelly lichen (*Collema spp.*) then the total site score would rise to 1 (0.5 + 0.5).

An additional metric based on all lichen species present was constructed from a similar method used in studying aquatic invertebrates (Hilsenhoff, 1982). The Modified Hilsenhoff Biotic Index (MHBI) assigns tolerance scores to each lichen taxa found in a cell and is calculated via,

$$MHBI = \frac{\Sigma ni\ ai}{T} \qquad (2)$$

where n is the number of ladder cells occupied by lichen i, a is the index value of that taxon (1 = pollution tolerant; 2 = intermediate tolerance; 3 = pollution intolerant), and T is the total number of ladder cells in the site (McMullin and Ure, 2008). The proportion of lichens of various scores permits a final site score between one (impacted) and three (unimpacted) to be calculated.

Lichen species by pollutant tolerance, species number and the IAP are shown in Table 2. The table is divided into those sites that experienced a winter median NO_2 concentration below 0.46 ppb and those sites above 0.46 ppb (highest median observed during the study) as a clear way of discerning which sites appear most impacted from local combustion sources. A similar division was not conducted for SO_2 as no significant difference ($p = 0.146$) was seen between the seasons for this metric.

2.3 Ogawa NO_2 and SO_2 PDS analysis

The two-sided Ogawa PDS contained one (two for duplicate) carbonate-coated quartz-fibre filter pad coated in tri-ethanolamine to adsorb both NO_2 and SO_2 (Ogawa, 2006). Un-opened filter pads obtained from Ogawa were stored in a freezer until required. The loaded PDS were placed inside an airtight Ziploc™ bag that was then placed inside an airtight transport container. The PDS in their transport containers were stored at 4°C before and after sampling. The PDS were kept on ice during transit to sampling sites and to laboratories for post sampling analysis.

Filter pads from the winter PDS were analyzed by RTI International (3040 Cornwallis Road, Building 6, RTP, NC, NC 27709) using an 8 mL water extract and ion chromatography, as specified by the Ogawa protocol for NO_2 and SO_2 (Ogawa, 2006). The summer PDS were analyzed in the Department of Process Engineering and Applied Science at Dalhousie University using a modified Ogawa protocol. The modified protocol included a reduction in the extraction volume to 1.8 mL, to improve sensitivity, and analysis of the nitrite (NO_2^-) and sulfate (SO_4^{2-}) anions simultaneously, effectively halving the ion chromatographic analysis time. This offers a significant enhancement of the Ogawa analysis protocol in terms of analysis time and improved sensitivity. The modified Ogawa protocol for the summer sampling period was as follows. Each filter pad was placed in a 25 mL screw-cap Nalgene bottle and 1.75 mL of 18 MΩ water and 0.05 mL of 1.75 % HPLC grade hydrogen peroxide solution (Fisher Scientific) added. The bottles were capped and the samples sonicated for 30 min. The extract was then filtered through an IC MILXLH, 13 mm diameter, 0.45 μm pore size syringe filter (Fisher Scientific) into autosampler vials. The solutions were analysed on a Thermo Fischer Scientific, Dionex ICS-1000 with an IonPac®, AG9-HC 4 × 50 mm guard and an IonPac®, AS9-HC 4 × 250 mm analytical column

for separation of NO_2^- and SO_4^{2-} anions. A 9 mM sodium carbonate eluent was used at a flow rate of 1 mL min^{-1}. An anion self-regenerating suppressor (ASRS® 300 4 mm) was employed in recycle mode during analysis. The injection loop was 100 µl. A seven-point standard curve was constructed to quantify the NO_2^- and SO_4^{2-} peaks. Three blank samplers were included in winter and summer and used for blank subtraction of sample values.

Average temperature and relative humidity for each sampling period were obtained from seven weather stations in the park. The data from the closest weather station was applied to each PDS site. These were used to determine the α-coefficient for calculation of exposure-average NO_2 and SO_2, as specified in the Ogawa protocol (Ogawa, 2006). The mean weather data associated with the NO_2 and SO_2 data at each sample site is presented in Table 3.

The NO_2 and SO_2 method detection limits (mdl) were calculated by multiplying the standard deviation of 17 replicates of the lowest measurable standard by the 99% Student's t-value. For the winter measurements NO_2 and SO_2 mdl were 0.11 and 0.09 ppb, respectively, whilst for the summer measurements they were 0.008 and 0.025 ppb, respectively. The lower detection limits obtained for the summer sampling was chiefly due to the reduction in the extraction volume used in the modified Ogawa protocol. Where NO_2 and SO_2 values were below their respective mdl, half the mdl value was substituted which is a standard approach when analyzing air quality data (Wheeler et al., 2011). This applied to 9 of the NO_2 measurements and 2 of the SO_2 measurements in winter, and to 0 and 2, respectively, of the measurements in summer.

PDS precision was quantified from the duplicate exposures at site A01GA via the expression $|PDS1-PDS2|/(PDS1+PDS2)$ (Wheeler et al., 2011). The bias in PDS NO_2 and SO_2 was determined during the summer deployment in the National Park by simultaneously collocating PDS with Federal Reference Method NO_x chemiluminescence and SO_2 pulsed fluorescence autoanalyzers in Halifax. Wintertime PDS bias was not determined. Bias was calculated as $(A-T)/T$, where A is the PDS NO_2 or SO_2 value and T is the true (autoanalyzer) value.

2.4 Statistical analyses

The results for NO_2, SO_2 and the weather variables are provided in Table 3 as mean values over the corresponding sampling period at each site. The descriptive statistics (SAS v9.2, SAS Institute Inc., Cary, NC 27513-2414, USA) for NO_2, SO_2 and weather data are contained in Table 4. WRPLOT View (Lakes Environmental, Waterloo, Ontario, N2V 2A9 Canada) was used to generate average wind vectors contained in Table 3. For comparative purposes, boxplots (SigmaPlot v12, Systat Software Inc., San Jose, CA 95110 US) of the mean exposure-averaged winter and summer NO_2 and SO_2 within the park, and in Port Hawkesbury and Sydney are shown in Figure 2 and 3. In order to understand the relationships between observed NO_2 and SO_2, weather variables, biological parameters, physical features and distance from upwind SO_2 sources correlation matrix analysis was conducted using IGOR Pro v6.22A (Wave Metrics, Inc., Portland, OR 97223, USA). The parameters investigated included all the weather variables, NO_2, SO_2, distance of the sampling sites to Sydney (DTS), IAP, species number (SN), old growth index (OGI), elevation (E), distance from road (DFR) and Modified Hilsenhoff Biotic Index (MHBI).

2.5 IAP predictive model

A multilinear regression model for IAP was developed using SigmaPlot v12.0. The independent variables used in the model included all of the winter and summer weather variables (rain fall, wind speed, wind direction, relative humidity, temperature), NO_2 and SO_2, DTS, SN, OGI, E and DFR. NO_2 and SO_2 were included because they were expected to be key predictors of IAP either directly or as surrogates of other phytotoxic chemicals associated with their emissions source such as HNO_3 and H_2SO_4. The inclusion of DFR, DTS and E in the model was to investigate associations of advection and dispersion of local and long-range sources of NO_2 and SO_2 to the IAP sites. The inclusion of OGI is because this metric is likely to be a strongly related to lichen number and diversity of species. The inclusion of SN and MHBI is because these biological variables are likely to be strong predictors of the IAP. The weather variables are included as they influence the fate and transport of air pollutants and growth of lichen species.

3. Results and discussion

3.1 PDS precision and bias

All duplicate NO_2 and SO_2 PDS exposures were above their mdl values. The winter and summer NO_2 precision was found to be 0.02 ppb and 0.13 ppb, respectively, and for SO_2 0.06 ppb and 0.20 ppb respectively. The PDS precisions determined in this study compare favourably with previous studies using Ogawa PDS; for example, an NO_2 precision of 0.07 ppb for a study in Windsor, Canada (Wheeler et al. 2011), and an SO_2 precision of 0.1 ppb in a study by Krupa and Legge (2000).

The PDS NO_2 bias in this study was 0.05 ppb, which again compares favourably with previous similar studies, e.g. between the bias of −0.17 ppb reported from a regional background site in China (Meng et al., 2010) and 0.17 ppb reported by Wheeler et al. (2011) for measurements in Windsor, Canada, and 0.012 ppb for a study in El Paso, USA (Sather et al., 2007). The PDS SO_2 bias here of −0.15 ppb is comparable with the bias of −0.19 ppb reported from a regional background site in China (Meng et al., 2010).

3.2 Seasonal and spatial NO_2, SO_2 concentrations and weather variables

The winter and summer NO_2, SO_2 concentrations and weather variables are presented in Table 3. Descriptive statistics of the winter and summer NO_2, SO_2 and weather variables across the individual sampling locations in Cape Breton National Park and the NAPS sites in Sydney and Port Hawkesbury are presented in Table 4. As described in Section 2.3, the large majority of measurements were above their respective mdl. Box-plots summarising the seasonal PDS measurements in the National Park, and comparing these to contemporaneous Government autoanalyser measurements in Sydney and Port Hawksebury, are shown in Figures 2 and 3 for NO_2 and SO_2, respectively.

From Table 4 the median (min−max) NO_2 concentrations in the park in winter and summer were 0.46 (0.12–2.46) ppb and 0.15 (0.01–0.35) ppb, respectively. For SO_2 they were 0.22 (0.10–0.59) ppb and 0.18 (0.04–0.40) ppb respectively. To place the results in context, the range of the winter and summer NO_2 and SO_2 concentrations in the park are significantly lower than those measured by Ogawa PDS in Sarnia "Chemical Valley", Canada where the ambient mean (and range) for NO_2 were 10.7 ppb (5.7 − 16.7 ppb), and for SO_2 were 3.4 ppb (0.8 ppb −13 ppb) (Atari et al.,

2008). Similarly, Table 4 shows that concentrations of NO_2 observed in the park were in the range 8 to 18 times lower than concentrations found in Sydney and Port Hawkesbury in both seasons. The higher NO_2 concentrations in the latter locations are presumably due to the substantially higher, and spatially widespread, combustion emissions for power, industry, transport, heating and cooking in these two urbanised areas (NPRI, 2010). The NO_2 observations made during the summer in the park are a factor of 10 lower than the NO_2 concentrations seen in Sequoia National Park, California in 1999 which ranged from 1.1 to 2.0 ppb (Bytnerowicz et al., 2002b). Bytnerowicz et al (2002a) also reports the range of NO_2 and SO_2 observed in 28 forests in the European Carpathian Mountains was 0.9 - 17.5 ppb and 2.1 - 6.3 ppb respectively, which ranges between 6 - 100 times greater than our NO_2 observations and ranging between 3.5 - 29 times greater for our SO_2 observations (Bytnerowicz et al., 2002a). The SO_2 concentrations in Port Hawkesbury (particularly in winter) were also significantly greater than those in the park, as were SO_2 concentrations in Sydney in winter. The high SO_2 concentrations in Port Hawkesbury point to the direct influence of a local source on that site at that time.

The mean winter and summer NO_2 (0.81 and 0.16 ppb) and SO_2 (0.24 and 0.21 ppb) concentrations in this Park are comparable to the NO_2 (0.6 ± 0.4 ppb) and SO_2 (0.7 ± 0.4 ppb) observed from a spatial study utilizing Ogawa PDS at a remote site on the Qinghai Plateau in China (Meng et al., 2010). These concentrations are not known to be directly phytotoxic to lichens (Fields and St. Clair, 1984; Nash-III, 1976), although observations from the current work are nevertheless indicative of an adverse association between air pollution and lichens, as discussed below. In respect of seasonality, the concentrations of NO_2 in the National Park in winter were significantly higher than in the summer (Kruskal-Wallis test, $p = 0.001$). It had been hypothesised that NO_2 concentrations would be higher in the summer due to greater tourist traffic

and photochemical production of NO_2. Instead, it is likely that increased local wood and fossil fuel combustion for space heating and from heavy equipment used in snow clearing, coupled to emissions into a lower boundary layer depth in the very cold winters, drives the significantly higher NO_2 concentrations observed in this season.

In contrast there was no significant difference (Kruskal-Wallis, $p = 0.429$) between winter and summer SO_2 concentrations in the park (Figure 3). This suggests a dominant influence for SO_2 concentrations from dispersion from long-range sources rather than local emissions into the local boundary layer. As can be observed in Figure 3, the SO_2 concentrations observed in the park during the winter are significantly lower than in Sydney ($p = 0.003$) and Port Hawkesbury ($p = 0.001$) and significantly lower in summer than in Port Hawkesbury ($p = 0.006$) (although not in Sydney ($p = 0.146$)) consistent with dispersion from a long-range source.

In terms of spatial variation within the park, Table 3 shows that the highest concentrations of NO_2 in both winter and summer are present in the Grand Anse Forest Valley (steep hill near "The Lone Shielding" crofters cottage), Rigwash (coastal road/view point/camp ground), the base of MacKenzie Mountain (coastal road/community of Pleasant Bay) and Neil Brook (coastal road/community of Neil's Harbour). The lowest NO_2 concentrations are confined to locations in the centre of the park that are far removed from local population centres and roads. This is consistent with the spatial pattern of NO_2 reflecting local vehicle emissions, and wood and fossil fuel combustion in local communities. Table 3 shows that NO_2 concentrations at sites A02GA, A03GA, A01GA and A04GA in the Grand Anse Valley were notably higher than at the other sites within the park. For example, NO_2 at site A03GA in winter was 2.46 ppb (summer 0.13 ppb), which was comparable to the town of Port Hawkesbury and about half that of the lower

range of NO_2 concentrations measured in the Canadian industrial city of Sarnia (Atari et al., 2008). The elevated NO_2 concentrations in the Grand Anse Valley are presumably associated with the local conditions that include a steeply inclined road running through a deep valley. Vehicle engines labour on both ascent and descent, which enhances emissions, and the physical constraint of the valley limits dispersion. It is also suspected that the valley acts as a "chimney" drawing air pollution from the Pleasant Bay community located at the base of the valley up into the Grand Anse valley. This community burns biomass for space and water heating in the winter and is a significant source of winter-time wood smoke (Ward et al, 2012).

Table 3 shows that whilst the NO_2 concentration at site A01CL in winter was below the mdl, in summer the NO_2 concentration (0.28 ppb) exceeded the majority of concentrations at other more remote locations of the park. Although relatively remote, this site is directly above the Highlands Links golf course that is not open during the winter. It is plausible that traffic emissions associated with use of the Links in summer maybe affected by a 'chimney effect' that draws NO_2 derived from the road and Links parking lot up the deeply incised valley, which is similar in topography to the Grand Anse Valley. If this is the case, it illustrates the important influence of local, tourist-related activity in an otherwise clean environment. Further monitoring of local weather conditions coupled with real-time monitoring of NO_2 at this site would be required to support this suggestion.

From Table 3 it appears that the temporal and spatial concentrations of SO_2 measured in the park were not associated with specific local sources. The potential upwind sources of SO_2 include Sydney which has two strong point sources (Lingan and Aconi Power stations, 60 km to the SE of the park). However, the correlations between SO_2 and distance to Sydney in the winter (R^2 =

0.2) and summer (R^2 = 0.1) are weak. Other significant upwind sources of S-fuel combustion in the region include the NewPage Paper Mill and Point Tupper power station in Port Hawkesbury, 120 km to the SW of the park and ship emissions along the park's coastline. The observation that winter and summer SO_2 concentrations tend to be associated with higher elevations in the park implies long-range transport from upwind sources rather than local emissions for this gas.

3.3. Associations with lichen species diversity

Table 2 shows that the number of pollutant intolerant lichen species drops from 10 to 5 with an associated decline in species number when the winter median NO_2 concentration is above 0.46 ppb and a summer median of 0.15 ppb. The presence of the intermediate tolerant lichen species when the median NO_2 is above 0.46 ppb is roughly unchanged but the species number is lower than when NO_2 concentration is below 0.46 ppb. Two of the pollutant tolerant species of lichen (*Phaeophyscia rubropulchra* and *Pyxine sorediata*) are absent from the sites that experience NO_2 concentrations above 0.46 ppb. However, two pollution tolerant species (*Parmelia sulcata* and *Melanelia subaurifera*) appear not to be impacted by median NO_2 concentrations above 0.46 ppb. From Table 2 it is clear that the IAP is lower for those sites that experience a median NO_2 concentration above 0.46 ppb. Four of the latter five sites are found within the Grand Anse Valley (an area suspected as being impacted by tourist traffic as discussed in section 3.2) with the remaining being a road side site along the Cabot trail. This information, together with the reduction in IAP, clearly demonstrates a relationship between the IAP, proximity to roads and areas of the park that experience poor air pollutant dispersion such as the Grand Anse valley.

The correlation matrix analysis of the air pollutants, weather variables, physical parameters and biological metrics yielded a number of positive and negative correlations with R^2 values ≥ 0.4,

including MBHI v IAP (R^2 = 0.98), MHBI v DFR (R^2 = 0.74), MHBI v SN (R^2 = 0.56), MHBI v DTS (R^2 = 0.67), DFR v IAP (R^2 = 0.75), IAP v SN (R^2 = 0.44), NO_2 v SN (R^2 = 0.44) and NO_2 v WS (R^2 = 0.41). The strong positive correlation between MHBI and IAP or SN is due to the very similar nature of these indices, i.e. measures of lichen species abundance. Of most importance in terms of the project objectives are the significant positive correlation between DFR v IAP (R^2 = 0.75) and a negative correlation between NO_2 v SN (R^2 = 0.44), which imply that lichen species density in this park is negatively associated with local traffic-related and other local combustion sources (as discussed in section 3.2).

A multilinear regression model to predict IAP in the park is provided in equation (3). The IAP can be predicted (model R^2 = 0.8) from the following linear combination of SN, OGI and DFR.

$$IAP = -0.641\ (\pm 0.21) + 0.0361\ (\pm 0.012) \times SN + 0.00848\ (\pm 0.0023) \times OGI + 0.000161\ (\pm 0.000027) \times DFR \quad (3)$$

Quoted uncertainty values in the coefficients are standard errors. The *p* values for the *constant*, *SN*, *OGI* and *DFR* variables were 0.008, 0.009, 0.002 and <0.001 respectively. The following variables were not significant predictors: wind speed, wind direction, rainfall, temperature, relative humidity, NO_2, SO_2, *MHBI*, *DTS*, and *E*.

The inclusion of OGI in the model is logical since lichen species diversity is expected to be greater in the old growth forest than newer forest stands. The inclusion of SN is also logical as it has a direct relationship with the IAP. The presence of the DFR variable in the model implicates

local, road associated pollution (incorporating acidic gases, particles and heavy metals) as being causative in the decline of lichen species diversity at sites with low IAP values. The exclusion of NO_2 and SO_2 from the model may be because it is long-term exposure to secondary acidic compounds (e.g. HNO_3 and H_2SO_4) formed from the primary NO_x and SO_2 emissions that are the true predictor rather than short-term exposure to NO_2 and SO_2. The multilinear regression model can be used to predict values of IAP elsewhere within the park using SN, OGI and DFR.

4. Conclusions

This work has provided new insights into the geospatial and seasonal variation of NO_2 and SO_2 in Cape Breton Highlands National Park, an area whose air quality has not previously been studied. It was observed that NO_2 concentrations in winter were significantly higher than those in summer, counter to the expectation that NO_2 concentrations would be higher in summer due to visitor traffic. SO_2 concentrations did not differ significantly between winter and summer. High NO_2 concentrations were observed in the Grand Anse Valley in both seasons, presumably due to the steep road and enclosed topography of this area reducing dispersion of traffic and local community related emissions. Multilinear regression predictors for a measure of lichen species diversity were lichen species number, forest old growth index and distance from road. The study has shown that local sources of air pollution appear to be the predominant influence on NO_2 concentrations and potentially also on the lichen species diversity in this National Park, especially in the Grand Anse valley. The study has shown that monitoring programs such as a lichen-based index of air purity can reveal locations where ecological detriment is occurring that may be associated with air pollution even at low levels. The implications from this work could be applicable to national parks elsewhere. The improved sensitivity to the Ogawa passive diffusion

sampler methodology developed here will also be applicable to other Ogawa PDS studies of ambient NO_2 and SO_2.

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Figure 1. Winter and summer NO_2 and SO_2 sampling locations in Cape Breton Highlands National Park

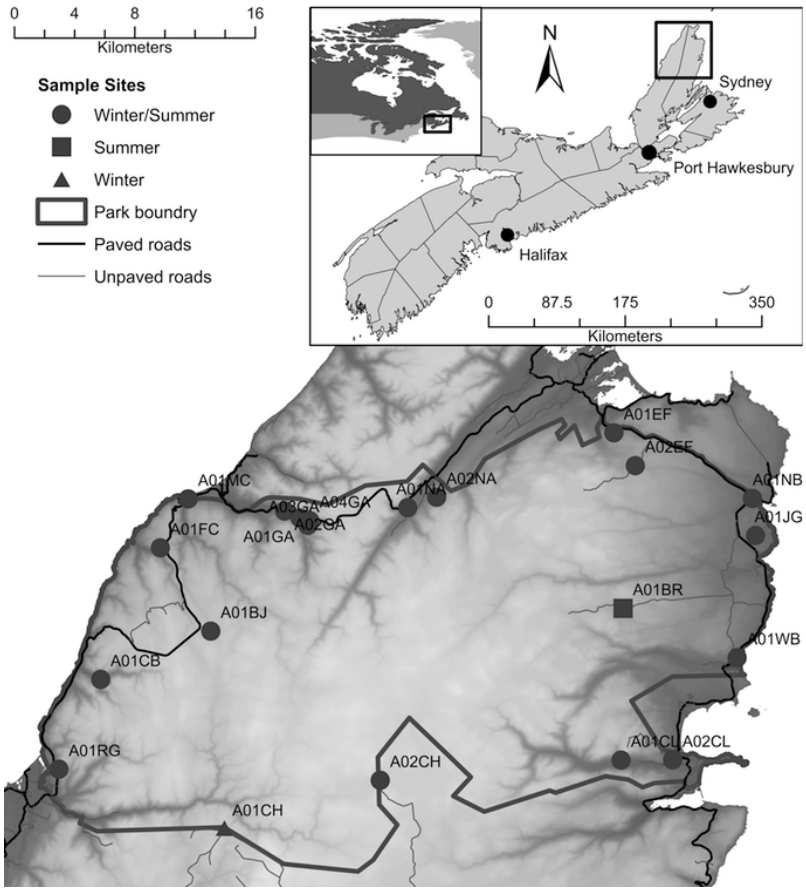

Figure 2. Boxplot of integrated winter and summer NO_2 concentrations found within the Park, Port Hawkesbury and Sydney

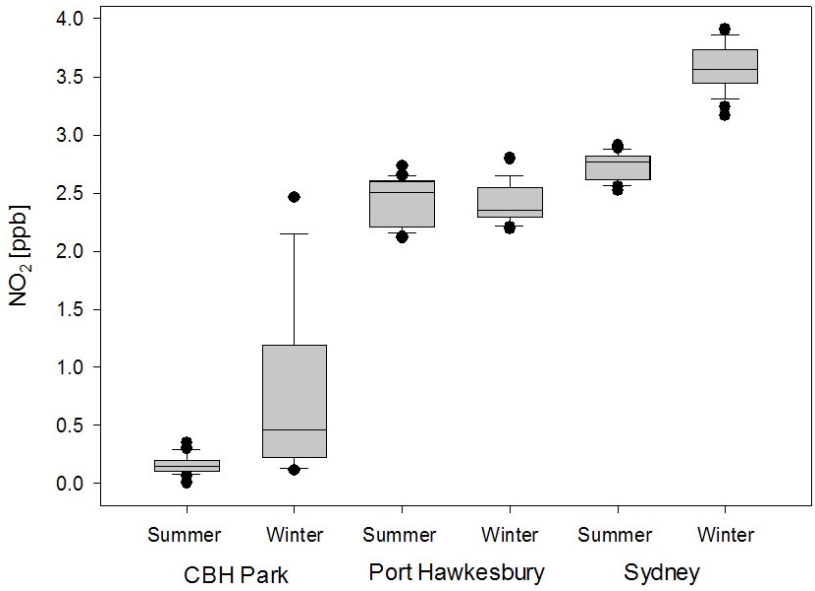

Figure 3. Boxplot of integrated winter and summer SO_2 concentrations found within the Park, Port Hawkesbury and Sydney

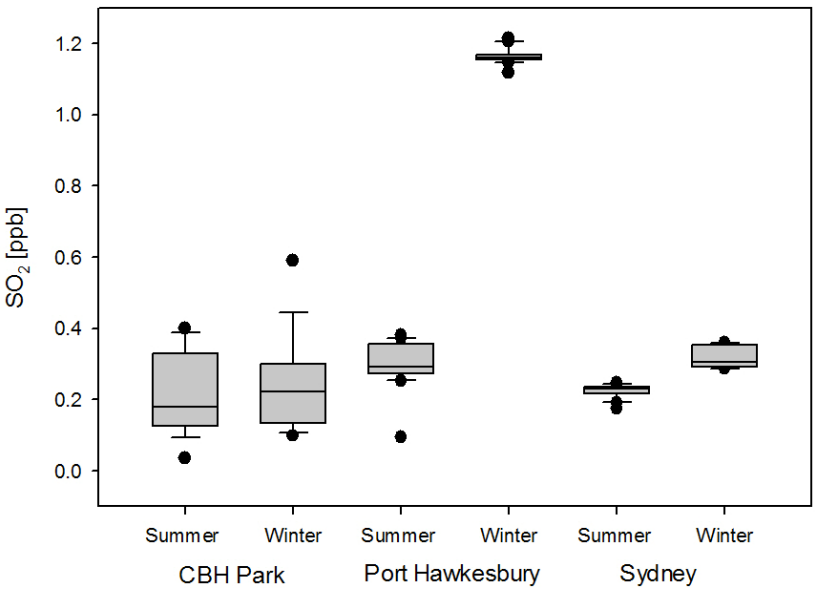

Table 1. Sampling site names, descriptions and coordinates. (W = Winter, S = Summer, EMAN = Ecological Monitoring and Assessment Network)

Site Name	Season Deployed	Site latitude / longitude d°mm'ss.s" NAD83	Description
A01BJ	W (lost) & S	N46 44 17.4 W60 48 36.9	Near Benjie's Lake
A01BR	S	N46 44 55.2 W60 27 01.8	Branch Pond
A01CB	W & S	N46 42 56.9 W60 54 29.1	Corney Brook EMAN site
A01CH	W	N46 37 30.2 W60 48 15.6	Park Spur Road, plateau
A01CL	W & S	N46 39 30.2 W60 27 30.0	Goldmine, EMAN site
A01EF	W & S	N46 51 12.3 W60 27 19.4	Effie's Brook EMAN site
A01FC	W & S	N46 47 34.9 W60 51 11.5	Fishing Cove EMAN site
A01GA	W & S	N46 48 30.3 W60 43 50.8	Grande Anse Forest Plot
A01JG	W & S	N46 47 22.1 W60 20 06.0	Jigging Cove Lake, east end.
A01MC	W & S	N46 49 18.1 W60 49 39.8	Base of Mackenzie Mountain
A01NA	W & S	N46 48 45.8 W60 38 12.9	EMAN site, base of North Mtn.
A01NB	W & S	N46 48 41.9 W60 20 11.8	Neil Brook, behind warden station
A01RG	W & S	N46 39 45.9 W60 56 47.1	Rigwash EMAN site
A01WB	W & S	N46 43 01.6 W60 21 16.4	Warren Brook, near Marrach
A02CH	W & S	N46 39 03.0 W60 40 04.2	Cheticamp Lake, park boundary
A02CL	W & S	N46 39 26.8 W60 24 48.8	Clyburn Valley
A02EF	W & S	N46 50 00.5 W60 26 15.6	Near Paquette Lake
A02GA	W & S	N46 48 46.4 W60 44 39.0	Grande Anse Forest Plot
A02NA	W & S	N46 49 06.2 W60 36 41.3	EMAN site, North Aspy
A03GA	W & S	N46 48 14.2 W60 43 27.2	Grande Anse Forest Plot
A04GA	W & S	N46 48 24.0 W60 43 20.9	Grande Anse Forest Plot

Table 2. Lichen species composition on ladder cells at study sites in Cape Breton Highlands National Park.

Species	Sites below winter median NO_2 0.46 ppb						Sites above winter median NO_2 0.46 ppb				
	A01CB	**A01CL**	**A01EF**	**A01FC**	**A01NA**	**A02NA**	**A01GA**	**A04GA**	**A02GA**	**A03GA**	**A01RG**
Index of Air Purity	0.37	1.13	0.13	0.46	0.37	0.69	0.16	0.40	0.00	0.53	0.07
Pollution Intolerant											
Cladonia sp.		3		1		21		4			
Collema subflaccidum		2		3							
Leptogium cyanescens	13	4		38		12		1			
Leptogium laceroides						1					
Lobaria pulmonaria	27	167	21	32	57	74	38	63		49	
Lobaria quercizans	42	78	9	35	27	51		23		78	17
Lobaria scrobiculata	3		2		2	2		4			
Nephroma laevigatum	2										
Parmeliella triptophylla					2	3					
Ramalina roeslerii						1					
Subtotal	87	254	32	109	88	165	38	95	0	127	17
Intermediate Tolerance											
Punctelia rudecta	17		25	18		3	1	4			27
Parmelia squarrosa	26	6	9	19		142	2	53	2	5	3
Subtotal	43	6	34	37		145	3	57	2	5	30
Pollution Tolerant											
Parmelia sulcata	43	5	222	65	92		108	40	111	71	44
Phaeophyscia rubropulchra		1		1		2					
Pyxine sorediata	3										
Parmelia sp.		3					1	1	1		4
Melanelia subaurifera	98	28	232	105	107	93	100	86	187	139	178
Subtotal	144	37	454	171	199	95	209	127	299	210	226

Table 3. Mean winter and summer NO_2, SO_2 and weather variables observed at the sampling sites.

	NO_2 *[ppb]*		SO_2 *[ppb]*		Temperature (ºC)		Relative Humidity (%)		Wind Direction (º)		Wind Speed (m/sec)		Rain (mm)	
Sample Site ID	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
A01BJ	0.06	<0.008	<0.025	sample lost	16.9	-4.6	86	95	272	237	3.5	0.0	3.9	3.0
A01BR	0.01	not sampled	0.40	not sampled	17.2	-2.4	79	82	284	332	2.3	3.1	5.8	4.6
A01CB	0.16	0.23	0.38	0.14	17.4	-0.7	81	80	184	284	4.5	6.8	4.5	3.0
A01CH	not sampled	<0.008	not sampled	0.34	N/A	-0.9	N/A	79	N/A	280	N/A	6.3	0.0	3.0
A01CL	0.28	<0.008	0.32	<0.025	17.9	-1.1	78	72	238	298	2.2	2.9	0.7	3.2
A01EF	0.21	<0.008	0.39	0.26	17.1	-2.9	85	78	211	327	2.3	3.1	5.8	3.8
A01FC	0.17	0.15	0.13	0.59	16.6	-4.9	87	95	263	237	3.6	0.0	4.2	2.9
A01GA	0.30	0.47	0.04	0.16	15.6	-3.9	84	89	251	297	4.3	6.2	4.8	2.9
A01GA (Duplicate)	0.23	0.45	0.06	0.18	15.6	-3.9	84	89	251	297	4.3	6.2	4.8	2.9
A01JG	0.19	<0.008	0.11	<0.025	16.9	-2.5	85	79	219	329	2.2	3.2	5.8	3.2
A01MC	0.18	1.19	0.17	0.10	17.3	-5.0	85	95	276	237	4.1	0.0	4.2	3.1
A01NA	0.11	<0.008	0.36	0.22	14.0	-4.1	86	91	255	304	4.4	6.2	6.1	3.2
A01NB	0.13	0.27	0.21	0.31	17.0	-2.4	84	79	232	329	2.2	3.2	1.7	3.2
A01RG	0.24	1.84	0.14	0.17	17.0	-0.6	81	80	179	283	4.5	6.8	4.9	3.0
A01WB	0.09	<0.008	0.25	0.11	16.8	-1.1	82	70	210	292	2.3	2.8	5.4	3.8
A02CH	0.09	<0.008	0.20	0.13	15.1	-4.1	85	89	253	301	4.3	6.0	5.4	5.3
A02CL	0.14	<0.008	0.19	0.11	16.9	-1.0	81	72	219	296	2.3	2.9	5.8	3.2
A02EF	0.10	0.12	0.13	0.41	16.9	-2.5	85	80	201	331	2.3	3.2	5.4	3.2
A02GA	0.15	0.89	0.10	0.27	15.6	-3.9	84	89	252	297	4.3	6.2	4.5	2.9
A02NA	0.14	<0.008	0.13	0.21	14.8	-4.1	84	91	261	304	4.4	6.2	5.6	3.2
A03GA	0.13	2.46	<0.025	0.29	15.8	-4.4	83	91	254	308	4.2	6.2	5.2	3.1
A04GA	0.35	0.46	0.17	0.29	15.6	-4.4	84	91	251	308	4.3	6.2	4.8	3.1

Table 4. Summary statistics of winter and summer NO_2, SO_2 and weather variables observed in Cape Breton Highlands National Park, Sydney and Port Hawkesbury

Pollutant	Season	Site	n	Mean	Median	Std Dev	Min	Max	Range
NO_2 *[ppb]*	Winter	CB Highlands	10	0.81	0.46	0.8	0.12	2.46	2.35
		Sydney	10	3.61	3.56	0.15	3.36	3.83	0.47
		Port Hawkesbury	10	2.39	2.34	0.11	2.27	2.55	0.28
	Summer	CB Highlands	20	0.16	0.15	0.08	0.01	0.35	0.34
		Sydney	20	2.73	2.77	0.12	2.52	2.91	0.39
		Port Hawkesbury	20	2.43	2.51	0.21	2.12	2.73	0.61
SO_2 *[ppb]*	Winter	CB Highlands	17	0.24	0.22	0.13	0.1	0.59	0.49
		Sydney	17	0.31	0.3	0.03	0.29	0.36	0.07
		Port Hawkesbury	17	1.17	1.16	0.02	1.12	1.21	0.1
	Summer	CB Highlands	18	0.21	0.18	0.11	0.04	0.4	0.36
		Sydney	18	0.22	0.23	0.02	0.17	0.25	0.07
		Port Hawkesbury	18	0.3	0.3	0.07	0.09	0.38	0.29
Temperature (ºC)	Winter	CB Highlands	-2.9	-2.9	1.5	-5.0	-0.6	4.4	-2.9
		Sydney	-1.5	-1.5	0.2	-1.9	-1.2	0.7	-1.5
		Port Hawkesbury	-1.6	-1.5	0.2	-2.0	-1.2	0.8	-1.6
	Summer	CB Highlands	20	16.4	16.9	1.0	14.0	17.9	3.8
		Sydney	20	17.9	17.8	0.5	17.1	18.7	1.6
		Port Hawkesbury	20	18.2	18.0	0.4	17.4	18.8	1.4
Relative Humidity (%)	Winter	CB Highlands	21	84	82	8	70	95	25
		Sydney	21	74	74	1	73	75	2
		Port Hawkesbury	21	76	76	1	75	77	2
	Summer	CB Highlands	20	83	84	2	78	87	9
		Sydney	20	83	83	1	80	84	5
		Port Hawkesbury	not available						
Wind Speed (km/h)	Winter	CB Highlands	21	15.0	11.6	8.4	0.0	24.6	24.6
		Sydney	21	20.0	20.0	0.4	19.3	20.7	1.4
		Port Hawkesbury	21	18.6	18.7	0.7	17.3	19.5	2.2
	Summer	CB Highlands	20	12.3	13.9	3.6	7.9	16.2	8.3
		Sydney	20	13.7	13.7	0.4	13.3	14.8	1.4
		Port Hawkesbury	20	12.7	12.7	0.3	12.3	13.4	1.1
Wind Direction (º)	Winter	CB Highlands	21	296	298	29	237	332	95
		Sydney	21	285	285	4	277	293	16
		Port Hawkesbury	21	297	297	4	291	302	11
	Summer	CB Highlands	20	238	251	30	179	284	105
		Sydney	20	211	213	8	197	228	31
		Port Hawkesbury	20	198	204	18	169	233	64